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(71) Applicant: MITSUI MINING COMPANY, LIMITED
1-1, Nihonbashi-Muromachi 2-chome
Chuo-ku Tokyo(JP)

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(71) Applicant: MITSUI MIIKE ENGINEERING CORPORATION
1, Aza Kayaba Koumachi
Tochigi-shi Tochigi-ken Tokyo(JP)

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(72) Inventor: Tsutsumi, Hiroshi
34-203, 8 Ootani-machi Wakamatsu-ku
Kitakyushu-shi Fukuoka-ken(JP)

(72) Inventor: Okamura, Morihito
1080, Tamura-cho
Tochigi-shi Tochigi-ken(JP)

(72) Inventor: Matsunaga, Oseamu
2008-22, Kurei Oohira-machi
Shimotsuga-gun Tochigi-ken(JP)

(74) Representative: Horton, Andrew Robert Grant et al,
BOULT, WADE & TENNANT 27 Furnival Street
London, EC4A 1PQ(GB)

(54) Process and apparatus for treating sulphur dioxide.

(57) A sulphur dioxide-containing gas, for example, obtained by a process using ammonia to remove SO_x and NO, is treated by the use of a reaction apparatus in which the gas is reduced and in which the composition of the gas is controlled by oxidation, to convert the composition of the gas into one suitable for the Claus reaction.

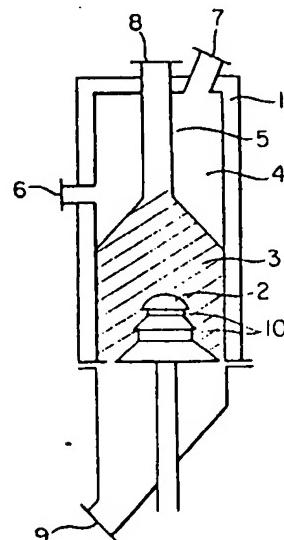


FIG. I

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"PROCESS AND APPARATUS FOR TREATING SULPHUR DIOXIDE"

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

This invention relates to the treatment of sulphur dioxide and particularly to the production of sulphur from gas containing sulphur dioxide. More particularly, it is concerned with treating a gas containing sulphur dioxide to convert it into a composition suitable for the Claus reaction process.

The production of elementary sulphur by a dry process comprising reducing sulphur dioxide sulphur and hydrogen sulphide and then obtaining elementary sulphur using a condenser and a Claus reactor has hitherto been carried out by bringing the gas containing sulphur dioxide (SO_2) into contact with a carbonaceous material such as coal, reducing and directly obtaining elementary sulphur, or by reducing SO_2 in the gas containing it to form hydrogen sulphide (H_2S) and then subjecting the resulting mixture gases of H_2S and SO_2 in a proportion of 2 : 1 to the Claus reaction to obtain sulphur.

In these processes, there have been proposed various methods of preparing raw material gases for the Claus reaction. One method comprises contacting a gas containing SO_2 with a carbonaceous material to reduce part of the SO_2 and thereby adjusting the ratio of H_2S and SO_2 to 2 : 1 (Japanese Patent Application OPI (Kokai) No. 167107/1982). Another method comprises dividing a gas containing SO_2 into two parts with a volume ratio of 2 : 1, reducing wholly the part with the larger volume to H_2S and mixing this with the other part to adjust the ratio of H_2S and SO_2 to 2 : 1 (Japanese Patent Application OPI (Kokai) No. 32307/1981). A third

method comprises reducing part or all of the SO₂ in
the gas containing SO₂ to obtain a gas containing
an excessive amount of H₂S and then subjecting the
gas to partial combustion in a combustion furnace
5 provided according to the method employed in the
desulphurization process for the ordinary petroleum
refining process to adjust the ratio of hydrogen
sulphide and sulphur dioxide to 2 : 1

10 The above described methods have various
disadvantages:

15 It is difficult to maintain constant a ratio of
hydrogen sulphide and sulphur dioxide by controlling
the reducing reaction. Moreover, a by-pass is
required. A gas containing sulphur dioxide in a high
concentration obtained by an SO_x and NO_x removal
process using ammonia, contains ammonia in a
proportion of up to 1.0 % in some cases.
Furthermore, after the reduction of the gas
containing SO₂ a part of the gas is then fed to a
20 combustion furnace in which the temperature is
maintained by the combustion of liquefied petroleum
gas. The conversion into sulphur dioxide is achieved
by feeding air in an excessive amount, thereby
controlling the ratio of H₂S and SO₂. It is
necessary to install a combustion furnace for
25 controlling the composition: the amount of the gas to
be processed is increased because of the use of the
excessive air, thus lowering the concentration of the
reaction components and the efficiency of the Claus
30 reaction.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an improved process for the production or
5 extraction of sulphur from a gas containing SO₂.

It is a further or alternative object of the present invention to provide an improved process for treating a gas containing SO₂ to convert the composition thereof into that suitable for the Claus
10 reaction.

According to one aspect the invention provides a process for treating a gas containing sulphur dioxide, comprising subjecting the gas to a reducing reaction and controlling by oxidation the composition of the gas to render the composition suitable for the
15 Claus reaction.

The invention also provides apparatus for treating a gas containing sulphur dioxide, comprising means for subjecting the gas to a reducing reaction and means for controlling the composition of the
20 reduced gas by oxidation.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic view of one embodiment
of an apparatus for treating a gas containing SO₂.

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Figure 2 is a schematic view of another
embodiment of an apparatus for treating a gas
containing SO₂.

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Figure 3 is a flow diagram to illustrate a
process for producing sulphur from a gas containing
SO₂ by the Claus reaction.

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Figure 4 is a schematic view of a further
embodiment of an apparatus for treating a gas
containing SO₂.

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DETAILED DESCRIPTION

The present invention is based on treating a
gas containing SO_2 by reduction and controlling the
composition of the gas by oxidation, preferably
performed in adjacent reactors or in the same reactor.

In the present invention, carbonaceous
materials such as coal and coke and reducing gases
such as carbon monoxide and hydrogen can be used as a
reducing agent and air or other oxygen-containing
gases can be used as an oxidizing agent.

In the apparatus shown in Figure 1, a gas
containing SO_2 is fed to a treatment apparatus 1
from an inlet 10, brought into contact with a
carbonaceous material at a temperature between 600 to
15 1000°C in a reducing part 3 filled with
carbonaceous material. About 80 to 100% of SO_2 in
the inlet gas is reduced to sulphur, hydrogen
sulphide, carbonyl sulphide, etc. The reducing part
20 3 is preferably a moving bed reactor filled with a
carbonaceous material supplied from an inlet 8 by way
of a chute 5. The resultant ash and non-fired
carbonaceous material are discharged from an exhaust
port 9. 2 represents a grate for discharging the
25 carbonaceous material.

The temperature of the reducing part 3 can be
maintained by feeding air or an oxygen-containing gas
separately or together with the raw inlet gas so as
to burn a part of the reducing agent.

30 The thus reduced gas is partially oxidized by
air fed from an air inlet 6 in a composition
controlling part 4 (combustion chamber) provided
above the reducing reaction part 3 preferably at a
temperature of 500 to 900°C to form sulphur oxide,
35 whereby the ratio of hydrogen sulphide and sulphur
dioxide, i.e. the value of $(\text{H}_2\text{S} + \text{COS})$ +

0.5CS₂)/SO₂ is adjusted to 1.50 to 2.50, preferably 1.90 to 2.10, suitable for the Claus reaction, and then discharged from a gas outlet 7. The rate of the oxidation reaction can be freely controlled by changing the quantity of air supplied.

5 Figure 2 shows another embodiment of an apparatus for treating a sulphur dioxide-containing gas according to the present invention, in which a composition controlling reactor 4 is adjacent to a reducing reactor 3, the other parts corresponding to 10 those described with reference to Figure 1.

When a combination of a carbonaceous material and a reducing gas is employed, the apparatus of Figure 1 or Figure 2 can be used as described. The 15 reducing gas may be supplied together with the gas containing SO₂ from the gas inlet 10. If a reducing gas is used alone, the temperature should be maintained by burning either a part of the reducing gas or fuel supplied for the purpose.

20 One example of a process for treating gas containing SO₂ is shown in Figure 3. A gas 26 containing SO₂ is fed to an apparatus 21 in which the gas is subjected to a partial or complete reduction of SO₂ then oxidized again to provide a 25 composition suitable for the Claus reaction, subjected to removal of by-produced sulphur in a condenser (not shown) and then fed to a Claus reactor 22. The condenser may be omitted. An air supply 23 provides air for the composition controlling reaction. The rate of air flow is being controlled by valve 24 according to the ratio of H₂S and the 30 other necessary components to SO₂ in a tail gas 29 of the Claus reaction. The ratio is determined by a meter 25.

35 Figure 4 shows a further embodiment of an apparatus for treating gas containing SO₂, the

apparatus comprising gas inlets 10 and 11 for raw material gas and reducing gas respectively, packing 12 such as broken bricks, a gas injection pipe 13, a fire grate 14, a combustion chamber 15 and a burner 16.

There are in general several advantages arising from the preferred practice of the invention. Since reduction and the control of composition by oxidization can be performed in a single reactor or 10 in a series of adjacent reactors, a combustion furnace for controlling the composition is not needed. Therefore, a supply of air for the combustion of liquefied petroleum gas, etc, is not required, so there is no increase of the process gas and the concentration of the reaction components can 15 be higher. Furthermore, the contact time with a catalyst in a Claus reactor can so be lengthened to improve the efficiency of recovery of sulphur. The tail or exhaust gas of the Claus reaction is decreased. Moreover, a temperature of 500 to 20 800 °C can readily be maintained by the combustion of combustible components in the reduced gas without using fuels such as liquefied petroleum gas. Furthermore, it is possible to control the furnace 25 temperature in the composition controlling part and the composition of the gas for the Claus reaction by controlling only the supply of air, control of the operation and composition is easy. In addition, whereas a gas containing SO_2 and obtained by a dry 30 process which removes SO_x and NO_x using ammonia contains up to 1% ammonia in some cases, according to the present invention gas can be treated such that the ammonia is substantially decomposed to give a low concentration, e.g. 500 to 1500 ppm, and a subsequent 35 Claus reaction is scarcely affected. Finally, a gas containing SO_2 and obtained by a process of

removing SO_x or SO_x and NO_x contains sulphur trioxide. However sulphur trioxide can be reduced by treating the whole gas according to the present invention and thus corrosion due to formation of

5 sulphuric acid can be prevented.

The following example is given in order to illustrate the present invention without limiting the same.

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Example 1

Using an apparatus as shown in Figure 1 and coke as a reducing agent, a raw material gas having a composition of 20-25% H_2O , 20-25% SO_2 , 25-35%
15 N_2 and 20-30% CO_2 was treated to produce sulphur according to the process as shown in Figure 3. The gas flow rate was 40-50 m^3/hr , the temperature in the reducing part was of 700 to 800°C , maintained by feeding air from the gas inlet 10 and burning the
20 reducing agent. The temperature in the past was 600 - 700°C and thus the gas for the Claus reaction was controlled to give an H_2S etc./ SO_2 ratio of 1.95 to 2.05. Sulphur was prepared with a yield of 90 to
25 95% and a purity of elementary sulphur of at least 99.99%.

Example 2

The procedure of Example 1 was repeated except that a gas having a composition of 40-45% H_2O ,
30 25-35% SO_2 , 15-20% N_2 and 10-15% CO_2 was treated at a gas flow rate of 55-60 m^3/hr , the reducing reaction temperature was $800-1000^\circ\text{C}$ and the composition controlling reaction temperature was
35 700 to 850°C , thus obtaining results of an H_2S etc./ SO_2 ratio of 1.95-2.05, sulphur recovery yield

of 93-97% and sulphur purity of at least 99.99%.

Example 3

5 Using an apparatus as shown in Figure 4 and a coke oven gas having a composition of 55% H₂, 30% CH₄, 7% CO, 1% O₂ and the balance N₂ and CO₂, a gas having a composition of 20-25% H₂O, 20-25% SO₂, 25-35% N₂ and 20-30% CO₂ was
10 treated to produce sulphur according to the process as shown in Figure 3. Flow rate of the raw material gas was 8 m³/hr, the reducing reaction temperature was 700 to 800°C and the composition controlling temperature was 600 to 700°C. The raw gas provided
15 for the Claus reaction was controlled to give an H₂S, etc./SO₂ ratio of 1.95 to 2.05. Sulphur was produced with a yield of 91 to 95% and a purity of at least 99.99%.

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CLAIMS:

- 5 1. A process for treating a gas containing sulphur dioxide which comprises subjecting the gas to a reducing reaction and controlling by oxidation the composition of the gas to render the composition suitable for the Claus reaction.
- 10 2. A process according to claim 1, wherein a carbonaceous material is used as a reducing agent.
- 15 3. A process according to claim 1 or claim 2, wherein a reducing gas is used as a reducing agent.
- 20 4. A process according to any foregoing claim, wherein the reducing reaction performed at a temperature between 600 and 1000°C.
- 25 5. A process according to any foregoing claim, wherein the oxidation is performed at a temperature distribution of 500 to 900°C
- 30 6. A process according to any foregoing claim, whereing the said composition is controlled so as to give a ratio of $(H_2S + COS + 0.5CS_2)$ to XO_2 of 1.5 to 2.5.
- 35 7. A process according to any foregoing claim in which the said composition is controlled essentially by the supply of air.
- 45 8. An apparatus for treating a gas containing sulphur dioxide, comprising means for subjecting the gas to a reducing reaction and means for controlling the composition of the reduced gas by oxidation.

9. Apparatus according to claim 8, wherein the said means are provided in the same reaction vessel.

5 10. Apparatus according to claim 8, wherein the said reducing means comprise a reducing reactor and an oxidizing reactor adjacent to each other.

10 11. Apparatus according to claim 8, wherein the means for subjecting the gas to a reducing reaction is a moving bed reactor employing carbonaceous material and the said means for controlling the composition is a combustion chamber above the moving bed reactor.

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FIG. 1

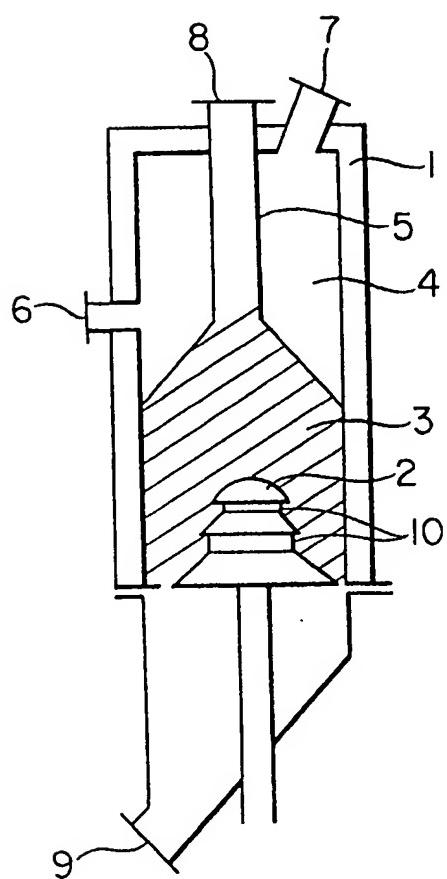
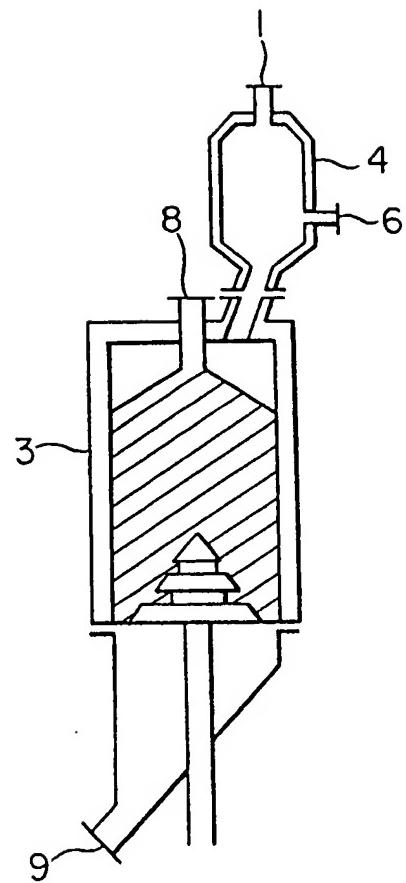


FIG. 2



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FIG. 3

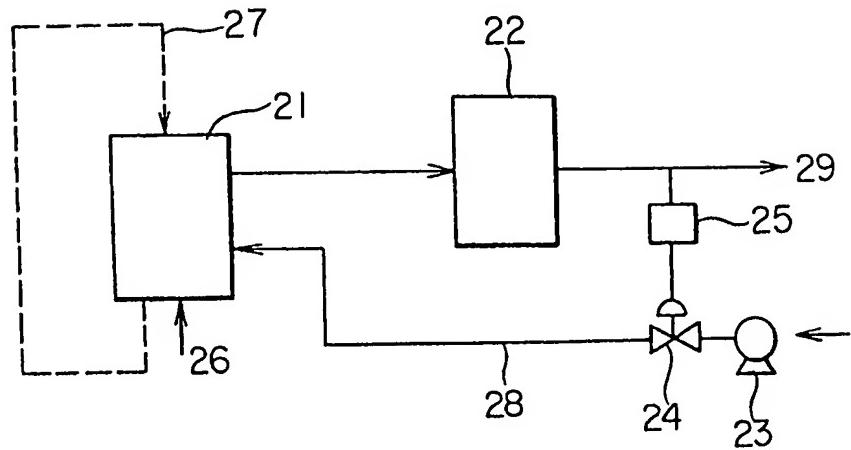


FIG. 4

